Quenching of Fluorenone Triplet by Amines

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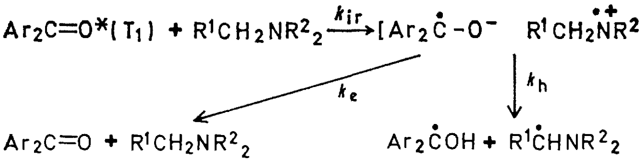
Summary Aniline, diphenylamine, and diazabicyclo-octane effectively retard photoreduction of fluorenone by triethylamine, by quenching the triplet of fluorenone; the efficiency of quenching by anilines is increased by electron-donating and decreased by electron-withdrawing *para*-substituents.

PHOTOREDUCTION of aromatic ketones by aliphatic amines shows moderately high quantum yields, and low sensitivity to concentration of amine and to diffusion-controlled quenchers.[1–3] These properties led us to suggest[1,2] initial rapid charge-transfer interaction between ketone triplet and amine, k_{1r}, followed either by charge destruction and quenching k_e, or by hydrogen transfer, k_h (Equation 1).



(1)

The value of k_{1r} increases in the order primary < secondary < tertiary amine,[3] while the quantum yield may reflect the relative importance of the alternative second steps, the observed photoreduction, k_h, and the postulated quenching, k_e. We have studied further the photoreduction of fluorenone to demonstrate the quenching of ketone triplets by amines. Fluorenone triplet is photoreduced with high efficiency by tertiary aliphatic amines in hydrocarbon solution, ϕ *ca.* 0·9, but with low efficiency, ϕ *ca.* 0·1, by a secondary amine, and with still lower efficiency by primary amines.[4,5] Fluorenone singlet is not quenched by primary aliphatic amines, but it is quenched by tertiary and secondary aliphatic amines and by aromatic amines,[5] presumably by an electron-transfer mechanism.[6] We now report quenching of fluorenone triplet by added amines, observed as retardation of photoreduction of the ketone by triethylamine.

Solutions of 0·00356 M-fluorenone and 0·0086 M-triethylamine in benzene, with and without added amines, were degassed and irradiated on a Bausch and Lomb 38-86-01 grating monochromator, Osram SP-200 lamp. Irradiations were at 366 or at 405 nm. Rates of photoreduction were determined from decrease in absorbance at 366 or 405 nm. Chemicals were obtained from commercial sources; they were recrystallized or redistilled before use, and showed melting or boiling points corresponding to literature values.

In preliminary experiments, aniline, diphenylamine, and the bicyclic diamine, 1,4-diazabicyclo-octane, with ionization potentials 7·7, 7·4, and 7·2 ev respectively,[7,8] retarded the photoreduction very efficiently when added in low, *ca.* 0·005 M, concentrations. However, triphenylamine, with I.P. = 6·9 ev,[9] but known to be a weak quencher for benzophenone,[10] was an ineffective retarder. Di-isopropylamine, I.P. = 7·7 ev,[11] retarded weakly, but to a degree consistent with the value of its k_{1r} with fluorenone, which is about 1/10 that of triethylamine.[4a] This indicates that the low quantum yield for photoreduction by the secondary amine arises from a low value of the k_e/k_h ratio. Primary aliphatic amines, isopropylamine, benzylamine, and t-butylamine led to very minor retardation, apparently because of high ionization potentials.[11]

The efficient retarders and a series of substituted anilines were studied quantitatively. Concentrations of added amine were low, 0·0002—0·004 M for the effective quenchers, so as to minimize singlet quenching. Ratios of rates of unquenched and quenched photoreductions were plotted against concentration of quencher, and slopes are given in the Table.

Retardation by amines of photoreduction of 0·0036M-*fluorenone by* 0·0086M-*triethylamine*

Quencher	$[\phi_0/\phi]$/M
1,4-Diazabicyclo-octane ..	1000
Diphenylamine	4800
Aniline	1200
p-Ethoxyaniline	7300
p-Methylaniline	4000
p-Bromoaniline	1740
p-Aminoacetophenone ..	625
p-Ethoxycarbonylaniline ..	125
p-Cyanoaniline	44

Values of k_q for quenching by these amines of the triplet state of fluorenone may be estimated, based on k_{ir} *ca.* 4×10^7 M^{-1} sec^{-1},[4a] and are in the range $0{\cdot}4$—3×10^9 M^{-1} sec^{-1} for the more efficient amines. 1,4-Diazabicyclo-octane is an efficient quencher, at the lower end of this range. The efficiency may be related to its low ionization potential[8] and relatively stable cation radical.[12] That it does quench is somewhat surprising since it is a photoreducing agent for *p*-aminobenzophenone.[2a] Aniline has similar quenching efficiency and diphenylamine is even more active. Amines with low ionization potential and no available α-hydrogen may be efficient quenchers for fluorenone. If they possess α-hydrogen, as do *NN*-dimethylaniline[13] and tertiary aliphatic amines,[4,5] they may act as photoreducing agents. These conditions may be necessary but not sufficient, since 1,4-diazabicyclo-octane quenches, triphenylamine does not quench efficiently, and di-isopropylamine does not photoreduce well. Electron-donating substituents, ethoxy and methyl, in the *para*-position, substantially increase values of k_q, while electron-attracting substituents, acetyl, alkoxycarbonyl, and cyano, lead to much less effective quenching. These results attest to the importance of electron availability and support charge-transfer interactions of triplet and amine, followed by charge destruction and quenching (Equation 2). They

$$\mathrm{Ar^1_2C{=}O^*(T_1) + Ar^2NH_2 \rightarrow [Ar^1_2\dot{C}\text{–}\overset{-}{O}\ \ H_2\overset{\cdot +}{N}Ar^2] \rightarrow Ar^1_2C{=}O + Ar^2NH_2} \qquad (2)$$

also support indirectly the suggestions[1,2] that photoreduction proceeds by a similar mechanism (Equation 1).

These compounds were also examined briefly as quenchers of the singlet state of fluorenone, by studying their effects on the intensity of fluorescence at 480 nm in benzene. Plots of ratios of fluorescence intensities in the absence and presence of 0·01—0·06 M-amine against concentration of amine were linear. All the compounds showed similar efficiencies, with slope values 40—80 M^{-1}, which, when combined with the singlet lifetime,[6] 3×10^{-9} sec, lead to values of $k_q = 2 \pm 0{\cdot}6 \times 10^{10}$ M^{-1} sec^{-1}, approaching diffusion control. The singlet, with excitation energy *ca.* 60·5 kcal, appears to interact indiscriminately with these amines.

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